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The structure of Bi_2NbO_5F and isomorphous compounds

By BENGT AURIVILLIUS

With 1 figure in the text

X-ray studies made previously on the compounds $CaBi_2Nb_2O_9$, $Bi_4Ti_3O_{12}$ and $BaBi_4Ti_4O_{15}$ (1) showed that they have very similar structures. The symmetry is tetragonal or pseudotetragonal, and the structures are each built up of quadratic Bi_2O_2 layers alternating with perovskite layers, the latter having different heights in the three different cases. The generalized formula for the compounds might be written Me_2O_2 $(Me'_{m-1}R_mO_{3m+1})$ where Me' is the 12 coordinated metal atom in the perovskite layers and R the 6 coordinated atom. The formulae for the above compounds, $Bi_2O_2(CaNb_2O_7)$, $Bi_2O_2(Bi_2Ti_3O_{10})$ and $Bi_2O_2[(BaBi_2)Ti_4O_{13}]$ thus have m values of 2, 3 and 4. The simplest case, $m=1$, would correspond to the formula $Me_2O_2(RO_4)$ and to a structure built up of Me_2O_2 layers and layers of RO_6 octahedra each octahedron sharing four corners. Compounds of this type have, however, not been successfully synthesized as yet.

The present paper deals with the compounds Bi_2NbO_5F, Bi_2TaO_5F and $Bi_2TiO_4F_2$, which correspond to the simplest case, $m=1$ above, except that some of the O atoms are replaced by F atoms. The formulae of the compounds might thus be written: $Bi_2(O, F)_2Nb(O, F)_4$ etc.

Preparation, powder photographs and analyses

Bi_2NbO_5F: When a mixture of BiF_3 and Nb_2O_5 in the mol ratio 4:1 was heated in air at 800° C for a short time, a few single crystals (very thin plates) were obtained. Powder photographs of this sample indicated a tetragonal unit cell with the same cell dimensions as would be expected for the above general type when $m=1$. The best conditions for the formation of this phase were then studied by heating 2.5 g mixtures ($2BiF_3+{}^1/_2Nb_2O_5$) in air at 640° C, this low temperature being chosen to reduce the volatility of the BiF_3. The reaction times were varied from 5–40 hours, and powder photographs were taken of each product. For reaction times of 7–15 hours the lines of the above tetragonal phase predominated in the powder photographs, the few extra lines were very weak (see Table 1).

The fluorine content was found to vary from 4.0 % (7 hours) to 2.4 % (15 hours), whereas the calculated value for Bi_2NbO_5F is 3.2 %. No variation in the size of the cell with the fluorine content was found, and it therefore seems probable that the composition of the phase is constant and that the observed variation in the F content is due to the presence of small impurities which are not visible in the powder photo-

Table 1

Powder photographs of Bi_2NbO_5F (sample with 2.8 % F)
Cr K radiation $\lambda_{Cr\,K_\alpha} = 2.2909$ Å

h k l	$10^4 \cdot \sin^2\theta_{calc}$	$10^4 \cdot \sin^2\theta_{obs}$	I_{obs}
1 0 3	1319	1332	st
0 0 6	1708	1711	m
1 1 0	1784	1795	m
1 1 2	1974	1969	vvw
1 0 5	2078	2083	vw
1 1 4	2543	2547	m
—	—	2785	vvw
0 0 8	3036	3033	w
—	—	3093	vw
1 1 6	3492	3490	st
2 0 0	3568	3567	st
2 0 2	3758	3754	vw
—	—	3808	vw
1 0 9 / 0 0 10	4734 / 4743	4737	st
1 1 8	4820	4827	w
2 1 3	4888	4891	st
2 0 6	5276	5292	m
2 1 5	5647	5658	w
1 1 10	6527	6529	vw
1 0 11	6631	6630	w
0 0 12	6830	6841	w
2 2 0	7137	7139	w
2 2 2	7327	7330	vw
3 0 1	8076	8080	vvw
2 1 9 / 2 0 10	8303 / 8311	8304	st
3 0 3	8456	8456	m
1 1 12	8614	8611	m
2 2 6	8845	8844	m
1 0 13 / 3 1 0	8908 / 8921	8919	m
3 1 2	9111	9119	vw
3 0 5	9215	9195	vw
0 0 14	9297	9292	vw

graphs. To check that the Bi/Nb ratio had not changed essentially during the heating, a complete analysis was made on one sample (9 hours heating). The following values were obtained as the mean of three analyses: Bi: 68.0±0.6%, Nb: 14.2±0.6%, F: 3.7±0.2%.

The values calculated for Bi_2NbO_5F are:

Bi: 68.5, Nb: 15.2%, F: 3.2%.

From these figures it seems probable that the formula of the compound is Bi_2NbO_5F.

Bi_2TaO_5F was prepared in exactly the same way as Bi_2NbO_5F. No analysis was made since the powder photographs were similar to those of Bi_2NbO_5F and niobium and tantalum compounds are usually isomorphous.

Fig. 1. C

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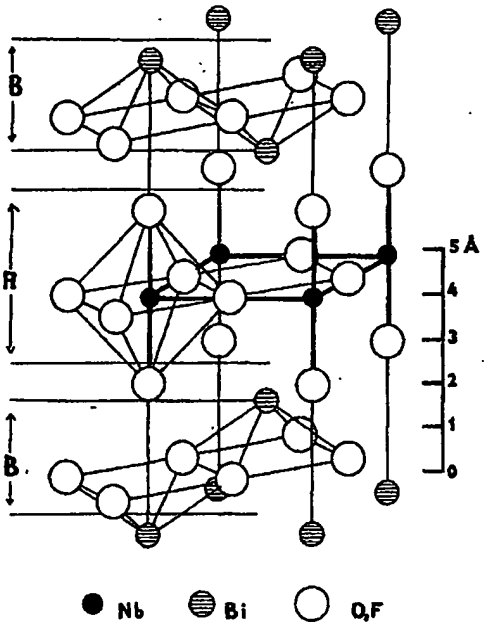

Fig. 1. One half of the unit cell of Bi_2NbO_5F. A denotes the region of $Nb(O,F)_4$ octahedra and B the $Bi_2(O,F)_2$ layers.

$Bi_2TiO_4F_2$: Mixtures of bismuth fluoride and titanium oxide in the mol ratio 2:1 (total 2.3 g) were heated in air at 640° for various lengths of thime. The powder photographs obtained from samples heated for 3 or 5 hours could be interpreted by assuming a mixture of BiOF (2) and a phase whose cell dimensions were nearly the same as those of Bi_2NbO_5F. (See Table 2, where the reflexions from the BiOF phase are designated by *b* and those from the other phase by *a*). The fluorine contents of the mixed samples were found to be 6.4 % (5 hours) and 8.4 % (3 hours) but no variation of the cell size with the fluorine content was found. The calculated values are 7.8 % for BiOF and 6.7 % for $Bi_2TiO_4F_2$. From the original Bi/Ti ratio, from the fluorine analysis and from the similarity of the powder photographs with those of Bi_2NbO_5F (Tables 1 and 2), it was concluded that the formula of the phase is $Bi_2TiO_4F_2$.

Methods of analysis: *Fluorine.* The samples were first decomposed by fusing with NaOH, and were then distilled with $HClO_4$ as described by WILLARD and WINTER (3). The distillate was titrated with $Th(NO_3)_4$ using Na-alizarinsulphonate as indicator.

Bismuth and Niobium. The samples were brought into solution, and niobium was determined as described in Scott's "Standard Methods" (4). Bismuth was first precipitated as Bi_2S_3, which was then redissolved, converted to Bi_2O_3 and weighed as such.

Unit cells and space group

The dimensions of the unit cells were determined from powder photographs taken with focusing cameras of the Phragmén type (Tables 1 and 2). The radiation used

Table 2

Powder photographs of $Bi_2TiO_4F_2$ (mixed with BiOF) *Cr K* radiation ($\lambda_{Cr\,K_\alpha} = 2.2909$ Å). *a* denotes the $Bi_2TiO_4F_2$ phase and *b* the BiOF phase

h k l	phase	$10^4 \sin^2\theta_{calc}$	$10^4 \sin^2\theta_{obs}$	I_{obs}
1 0 1	*a*	957	941	vvw
1 0 1	*b*	1270	1265	m
1 0 3	*a*	1351	1354	st
0 0 2	*b*	1352		
0 0 6	*a*	1771	1767	m
1 1 0	*a*	1816	1811	m
1 1 0	*b*	1864	1858	vvw
1 1 2	*a*	2013	1999	w
1 0 5	*a*	2138	2132	w+
1 0 2	*b*	2284	2288	vvw
1 1 4	*a*	2603	2601	m
–	–	—	3074	vw
1 1 2	*b*	3216	3231	w
1 0 7	*a*	3319	3320	vw
1 1 6	*a*	3587	3600	st
2 0 0	*a*	3631	3624	st
2 0 0	*b*	3728	3744	w
2 0 2	*a*	3828	3822	w
1 0 3	*b*	3974	3982	w
–	–	—	4352	vvw
2 0 4	*a*	4418	4426	vvw
2 1 1	*a*	4588	4590	w
–	–	—	4674	vvw
1 0 9	*a*	4893	4904	st
1 1 3	*b*	4906		
0 0 10	*a*	4919		
2 1 3	*a*	4982	4979	st
2 0 2	*b*	5080	5084	w
2 0 6	*a*	5402	5416	m+
0 0 4	*b*	5408		
2 1 5	*a*	5769	5768	m
2 1 2	*b*	6012	6025	m
1 0 4	*b*	6340	6353	w
2 0 3	*b*	6770	6786	m
2 0 8	*a*	6779		
1 0 11	*a*	6860	6869	m
2 1 7	*a*	6950	6950	vvw
0 0 12	*a*	7084	7075	m
2 2 0	*a*	7262	7262	m
1 1 4	*b*	7272		
2 2 0	*b*	7455	7456	w
2 2 2	*a*	7459		
2 1 3	*b*	7702	7709	m
–	–	—	8049	vw
3 0 1	*a*	8210	8210	vw
–	–	—	8352	vw
2 1 9	*a*	8524	8524	st
2 0 10	*a*	8550		
3 0 3	*a*	8613	8603	m
3 0 1	*b*	8736	8725	w
2 2 2	*b*	8814	8807	w
1 1 12	*a*	8900	8900	m

Table 2 (continued)

hkl	phase	$10^4 \sin^2\theta_{calc}$	$10^4 \sin^2\theta_{obs}$	I_{obs}
2 2 6	a	9033	9027	m
3 1 0	a	9078	9072	w
2 0 4	b	9136	9136	vw
3 1 2	a	9275	9272	m
3 1 0	b	9319	9319	w
1 0 5	b	9382	9384	m
3 0 5	a	9400		

was $Cr\,K$ ($\lambda_{Cr\,K_\alpha}$=2.2909 Å). As mentioned above the powder photographs could be interpreted by assuming tetragonal unit cells; the cell dimensions are given below.

	a (Å)	c (Å)
Bi_2NbO_5F	3.835	16.63
Bi_2TaO_5F	3.829	16.64
$Bi_2TiO_4F_2$	3.802	16.33

The errors in these figures are estimated to be ±0.1 %.

The observed density was 8.0 for Bi_2NbO_5F (preparation with 2.8% F), which agrees fairly well with the assumption of 2 formula units per unit cell, giving a calculated density of 8.26.

Zero and first order Weissenberg photographs around the a axis were taken. There was nothing in the Weissenberg photographs to indicate a Laue symmetry lower than D_{4h}—4/mmm. The only extinctions found were that h, k, l were absent for $h+k+l$ odd, which is characteristic of the space groups C_{4v}^9, D_{2d}^9 D_{2d}^{11} and D_{4h}^{17}.

Powder photographs only were taken of the compounds Bi_2TaO_5F and $Bi_2TiO_4F_2$, and from these it was concluded that these substances are isomorphous with Bi_2NbO_5F.

Positions of the metal atoms

Bi_2NbO_5F: With 2 formula units per unit cell there are 4 Bi and 2 Nb atoms per unit cell. The intensities of the spots in the Weissenberg photographs seemed in the main to depend only on the l values. Thus for l even $I_{00l} \approx I_{11l} \approx I_{20l}$ etc. and for l odd: $I_{10l} \approx I_{21l} \approx I_{30l}$ etc. With these intensity values a good approximation of the Patterson-Harker function along $00z$ could be obtained by using only the intensity values of $h0l$ and $h1l$. The Patterson-Harker function thus calculated (not given here) showed only one, big, maximum, at z=0.34. This maximum, and the absence of others, could be explained only by assuming that 4 Bi atoms are situated at the positions $\pm 00z$ with z=0.17 or z=0.33, and the Nb atoms at the positions $00\frac{1}{2}$ or 000. Arbitrarily choosing 000 as the position for Nb, trial and error calculations gave the value 0.325 for the Bi parameter.

No determination of z_{Bi} was made for **Bi_2TaO_5F**.

For **$Bi_2TiO_4F_2$** the powder photograph data were used to determine the Bi parameter. Assuming the Ti atoms to be situated at 000 and the O and the F atoms to occupy the same positions as given below for Bi_2NbO_5F, the value z_{Bi}=0.327±0.006 was obtained from trial and error calculations.

Table 3

Weissenberg photographs of Bi_2Nb

Zero layer

	h k	0 0		2 0		4 0	
l		I_{calc}	I_{obs}	I_{calc}	I_{obs}	I_{calc}	I_{obs}
0		—	—	170	vst	37	w
2		—	—	10	w	3	vw
4		0.3	—	0.04	—	0.05	—
6		220	vst	67	w	34	vw
8		12	w	5	vw	6	vvw
10		3	vw	2	—	2	—
12		44	st	26	w	86	st
14		15	m	11	w		
16		10	w	10	w		
18		16	m	28	m		
20		22	m				

	h k	1 0		3 0	
l		I_{calc}	I_{obs}	I_{calc}	I_{obs}
1		7	w	1	vw
3		270	vst	42	w
5		40	w	8	vw
7		1	—	0.2	—
9		75	m	30	vw
11		18	w	10	vw
13		3	vw	3	vw
15		20	m	19	m
17		12	w		
19		14	w		

Positions of the O and the F atoms

The positions of the O and the F atoms could not be distinguished either from the diffraction data, or from space considerations because of the similarity in the reflecting power and ionic radii of O^{2-} and F^-. The problem is therefore treated as though O and F were the same atomic species. In the following, the O and the F atoms are denoted by (O, F) and the discussion relates to Bi_2NbO_5F for which z_{Bi} could be accurately determined from the Weissenberg photographs.

It seemed reasonable to assume that the Nb atoms are surrounded by a regular or nearly regular octahedron of (O, F) atoms with distances Nb–(O, F) ≈ 2.0 Å. Neglecting the polar space group C_{4v}^9, these conditions are fulfilled only if 4 (O, F) atoms, here called $(O, F)_1$, are situated at the positions $\pm 00z$ with $z \approx 0.12$, and 4 (O, F) atoms, $(O, F)_2$, at the positions $0\frac{1}{2}0$, $\frac{1}{2}00$. Assuming the distance (O, F)–(O, F) to be ≥ 2.5 Å and the distance Bi–(O, F) to be ≥ 2.2 Å there is only room for the remaining 4 (O, F) atoms, $(O, F)_3$, at the positions $0\frac{1}{2}\frac{1}{4}$, $\frac{1}{2}0\frac{1}{4}$.

Table 3. Bi_4NbO_5F *Cu K α* radiation photographs

First layer

	h k	1 1		3 1	
l		I_{calc}	I_{obs}	I_{calc}	I_{obs}
0		210	vst	36	w
2		17	w	4	vvw
4		11	w	2	—
6		110	m	33	w
8		27	vw	9	vw
10		2	vvw	1	—
12		21	m	20	w
14		14	w	20	w
16		5	w	17	w
18		19	m		
20		58	st		

	h k	0 1		2 1		4 1	
l		I_{calc}	I_{obs}	I_{calc}	I_{obs}	I_{calc}	I_{obs}
1		7	—	2	vw	1	vvw
3		270	vst	74	m	33	w
5		40	m	13	w	7	—
7		1	—	0.3	—	0.2	—
9		75	vst	40	w	53	w
11		18	m	12	vvw	51	w
13		3	vw	3	vw		
15		20	m	19	m		
17		12	w	19	m		
19		14	w				

The coordination and distances in Å will be:

Bi–4 $(O, F)_3 = 2.29$	Nb–2 $(O, F)_1 = 2.0$
Bi–4 $(O, F)_1 = 2.9$	Nb–4 $(O, F)_2 = 1.92$
$(O, F)_3$–4 $(O, F)_3 = 2.71$	$(O, F)_2$–4 $(O, F)_2 = 2.71$
$(O, F)_1$–4 $(O, F)_3 = 2.9$	$(O, F)_1$–4 $(O,F)_2 = 2.8$

The proposed structure is given in the summary. Calculated and observed intensities for the reflexions in the Weissenberg photographs are given in Table 3. I_{calc} is derived as follows:

$$I_{calc} = \frac{1 + \cos^2 2\theta}{1600 \cdot \sin 2\theta} \cdot F^2 \text{ where } F = \sum f \cos 2\pi (hx + ky + lz).$$

The lines of maximum absorption in the Weissenberg photographs (see 5) are indicated by dotted lines in Table 3. If the absorption effects are taken into account, the agreement between calculated and observed intensities is quite good.

Discussion of the structure

Even if the $(O, F)_1$ atoms (see above) are assumed to occupy such a position that the distance Bi–4 $(O, F)_1$ is as small as possible [z $(O, F)_1 = 0.15$, $(O, F)_1$–$(O, F)_3 = 2.5$, Nb–2 $(O, F)_1 = 2.5$, Bi–4 $(O, F)_1 = 2.7$], the distance Bi–4 $(O, F)_1$ will still be much longer than the distance Bi–4 $(O, F)_3$. It therefore seems appropriate to describe the structure of Bi_2NbO_5F as being built up of $Bi_2(O, F)_2$ layers alternating with octahedral layers having the composition $Nb(O, F)_4$, both layers being perpendicular to the c-axis. It might be pointed out that the structure of $Bi_2(O, F)_2Nb(O, F)_4$ is basically of the same type as the "X_1 structures", Me_2O_2X, previously investigated by SILLÉN (6). Thus the octahedral sheets $Nb(O, F)_4$ correspond to single layers of halogen atoms, X, in Me_2O_2X.

Discussion of the distribution of the O and the F atoms

As seen above, the distance Bi–4$(O, F)_3$ is 2.29 Å for Bi_2NbO_5F. For $Bi_2TiO_4F_2$ the corresponding distance is calculated to be 2.26 ± 0.06 Å. These distances are very nearly the same as the corresponding distances, Bi–4 O, within the Bi_2O_2 layers of other bismuth oxicompounds (6). This need not, however, necessarily mean that the $Bi_2(O, F)_2$ layers (see the figure) are free from F atoms, since compounds with $Bi_2(O, F)_2$ layers which certainly contain F atoms have not been investigated hitherto, and thus the distances within such layers are unknown.

For the present it seems therefore best to make no special assumptions as to the distribution of the O and F atoms.

SUMMARY

The crystal structure of Bi_2NbO_5F has been investigated by means of Weissenberg and powder photographs. From powder photographs the compounds Bi_2TaO_5F and $Bi_2TiO_4F_2$ have been found to be isomorphous with Bi_2NbO_5F. The following structure is proposed for Bi_2NbO_5F:

D_{4h}^{17}–$I\,4/mmm$

$(000, \frac{1}{2}\frac{1}{2}\frac{1}{2})+$

2 Nb	in 2 (a) : 000	
4 Bi	in 4 (e) : $\pm 00z$	$z = 0.325 \pm 0.001$
4 $(O, F)_1$	in 4 (c) : $0\frac{1}{2}0$, $\frac{1}{2}00$	
4 $(O, F)_2$	in 4 (e) : $\pm 00z$	$z = 0.12 \pm 0.01$
4 $(O, F)_3$	in 4 (d) : $0\frac{1}{4}\frac{1}{4}$, $\frac{1}{2}0\frac{1}{4}$	

The cell dimensions are $a = 3.835$ Å, $c = 16.63$ Å for Bi_2NbO_5F. The positions of the metal atoms were determined from the diffraction data, those of the (O, F) atoms from space considerations. Although it does not seem improbable that O atoms alone occupy the positions $0\frac{1}{2}\frac{1}{4}$, $\frac{1}{2}0\frac{1}{4}$, Bi and O thus forming Bi_2O_2 layers as in other bismuth oxicompounds, nothing can be definitely stated as to the distribution of the O and F atoms.

The structure is built up of quadratic $Bi_2(O, F)_2$ layers alternating with octahedral sheets having the composition $Nb(O, F)_4$ (see figure) and the formula might thus be written: $Bi_2(O, F)_2Nb(O, F)_4$. The structure is formally related to a series of

previously investigated structures of general formula Me_2O_2 ($Me'_{m-1}R_mO_{3m+1}$) and represents the simplest case of this series, i.e. $m=1$.

University of Stockholm, Institute of Inorganic and Physical Chemistry, May 1952.

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